ESRF	**Experiment title:** RXS investigation of doping-dependent charge superstructures in single-layer La2-xCaxCoO4 (x=0.4, 0.5, 0.6).	**Experiment number**: HC2526
Beamline: BM02	**Date of experiment**: from: 29/06/2016 to: 05/07/2016	**Date of report**: 25/02/2021
Shifts: 18	**Local contact(s)**: Guillaume Beutier	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Joaquín García[1]*, Javier Blasco[1]*, Gloria Subías[1*], Vera Cuartero[2], Sara Lafuerza[2], Javier Herrero-Martín[3] and J. L. García-Muñoz[4]

[1] Instituto de Ciencia de Materiales de Aragón. Plaza San Francisco n.9 CP 50009. Zaragoza (Spain)
[2] ESRF, 71 avenue des Martyrs CS 40220 FR - 38043 Grenoble Cedex 9
[3] ALBA synchrotron, Carretera BP 1413, Km. 3.3, 08290 Cerdanyola del Vallès (Spain)
[4] Instituto de Ciencia Materiales de Barcelona. Campus UAB Bellaterra ES - 08193 Bellaterra (Spain)

Report:

The aim of this proposal was to provide a quantitative determination of the Ca-doping dependence of charge disproportionation order of cobalt atoms in the doped $La_{2-x}Ca_xCoO_{4\pm\delta}$ ($0.4 \leq x \leq 0.7$) series. We have performed the complete (energy, azimuth angle and polarization dependencies) RXS study at the Co K-edge in three single crystals of the Ca system ($La_{1.6}Ca_{0.4}CoO_4$, $La_{1.4}Ca_{0.6}CoO_4$ and $La_{1.4}Ca_{0.7}CoO_4$) at room temperature in order to determine the type of commensurate/incommensurate charge ordering that takes place for $x<0.5$ and $x>0.5$[1].

The three single crystals show RXS at (3/2, 3/2, 0) and (5/2, 5/2, 0) reflections confirming the presence of an alternating checkerboard pattern in their charge ordered phases. Figure 1 shows the energy depedence of the (3/2, 3/2, 0) superstructure reflection for $La_{1.6}Ca_{0.4}CoO_4$ and $La_{1.4}Ca_{0.6}CoO_4$ compared to that observed in the half-doped $La_{1.5}Ca_{0.5}CoO_4$ for two values of the azimuth angle, $\varphi=90^o$ and $\varphi=0^o$ (fig. 1a). Qualitatively, the three samples show similar energy and azimuthal dependencies. In Fig. 1(a), we note an energy shift of the main resonance peak depending on the azimuth angle. In this way, the peak occurs at ~7.725 keV for $\varphi=90^o$ (**E**//**c)** and about 2 eV above for $\varphi=0^o$ (**E**⊥**c)**. On the other hand, some differences are noticeable in the intensity of the main resonance. As can be seen in Fig. 1(a), the $I_{\mathbf{E}//\mathbf{c}}$ / $I_{\mathbf{E}\perp\mathbf{c}}$ ratio for the $(3/2, 3/2, 0)_t$ reflection is 2, 1.5 and 1.8 for x=0.4, 0.5 and 0.6 samples, respectively. The lowest difference in the peak intensity as a function of the azimuth angle is then shown by the nominal half-integer valence (x=0.5) sample. Moreover, Fig. 1(b) displays the energy-dependent spectra of the $(1/2, -1/2, 9)_t$ and $(1/2, 1/2, 10)_t$ reflections for the $La_{1.3}Ca_{0.7}CoO_{3.9}$ crystal. In this case, the electric field polarization vector **E** is nearly parallel to the *ab*-plane and a different sign in the interference between the Thomson scattering and the resonant scattering of Co atoms occurs for *l* odd (destructive) or even (constructive) in the σ–σ' channel. We note that these reflections of the x=0.7 sample do not show azimuthal dependence, as expected from the fact that **E** lies close to the *ab*-plane (within 8º) and the lack of anisotropy in the *ab*-plane.

It is noteworthy that we do not find resonant superlattice $(h\pm\varepsilon, h\pm\varepsilon, 0)_t$ reflections with a modulation $2\varepsilon=1-x$ in the $La_{2-x}Ca_xCoO_{4\pm\delta}$ samples (x=0.4, 0.6 and 0.7) opposite to the results found in layered manganites, where the observed resonant reflections exhibited a modulation vector following the doping rate.[2] Instead, here layered cobaltites show a strong stabilization of the $(h/2, h/2, 0)_t$ reflection well out of the

nominal doping x=0.5, in agreement with previous reports.[3] This result reflects different structural effects of the hole doping for both layered structures.

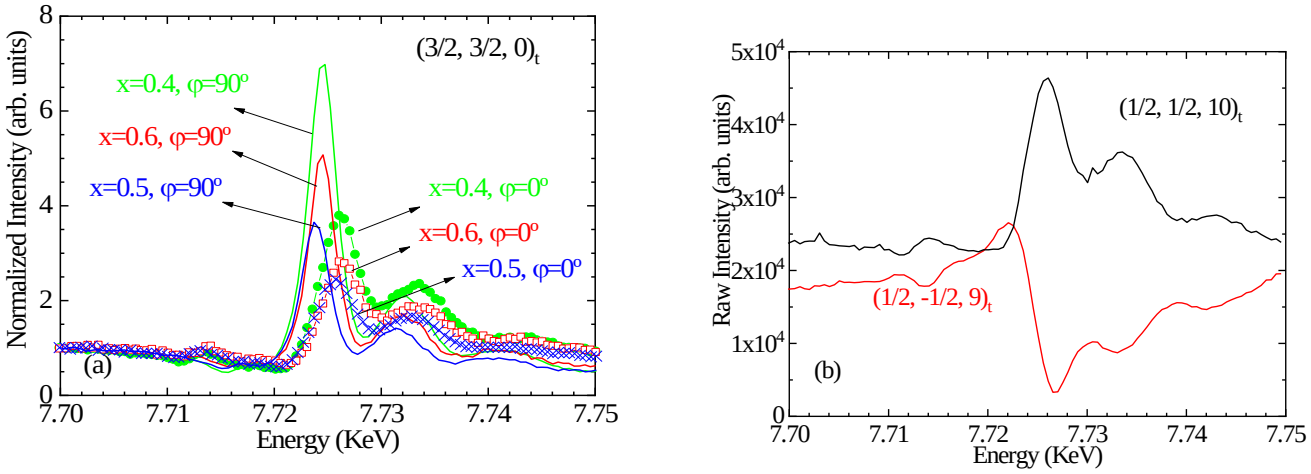

Figure 1. (a) Energy dependence of the RXS intensity of the (3/2, 3/2, 0) reflection in the σ-σ' polarization channel for different azimuthal angles in $La_{2-x}Ca_xCoO_{4\pm\delta}$ (x=0.4, 0.5, 0.6) samples. (b) Energy dependence of the resonant $(1/2, -1/2, 9)_t$ and $(1/2, 1/2, 10)_t$ reflections for the $La_{1.3}Ca_{0.7}CoO_{3.9}$ sample at φ=90º in the σ-σ' channel.

In addition to the same azimuthal dependence of the $(h/2, h/2, 0)_t$ reflection exhibited by the three samples with a π-periodicity for the σ–σ' scattered intensity, being the maximum intensity observed at φ=90º (**E**//**c**), for the σ–π' scattered intensity, the three samples also show a π/2 periodicity with the maximum intensity at φ=45º. Therefore, a single theoretical model should be able to describe the RXS properties of the three samples.

To analyze the resonant x-ray data, a new semi-empirical method has been proposed[1]. The real part of the resonant structure factor can be obtained by the subtraction of the experimental RXS spectra of two resonant (*h*/2, *h*/2, *l*)-type reflections with identical resonant structure factor that either adds or subtracts to the Thomson term depending on the *h*-index. This simple approach in combination with conventional XANES spectra has allowed us to obtain the site-resolved XANES spectra (or the imaginary part of the resonant atomic scattering factors) for the two non-equivalent Co sites, which results in a charge disproportionation of about 0.6 e^- in the ordered phases.

Finally, we found the pattern of small distortions (~ 0.05 Å) around the two Co sites compatible with the resonant x-ray scattering results. The symmetry of this displacement pattern is consistent with the *A2mm* (or *Ammm*) orthorhombic structure of the ordered phase and the structural transition is accounted for by the condensation of two soft modes $-X_1^+(B_{2u})$ and $X_1^+(A_1)$ – acting on the oxygen atoms, which results in the checkerboard ordering formed by alternating expanded and compressed CoO_6 octahedra,

In conclusion, $La_{2-x}A_xCoO_{4\pm\delta}$ series seem to maintain the checkerboard ordering of only two sites for all compositions with x≠0.5. The reason is that the hole-doping does not follow the Ca content in the $La_{2-x}A_xCoO_{4\pm\delta}$ series but the average Co valence state is modulated by the oxygen stoichiometry in such a way that all the samples from x=0.4 up to 0.7 have very similar Co valence state close to the $Co^{+2.5}$.

References

[1] J. García et al., Phys. Rev. B **97**, 085111 (2018)
[2] J. García et al., Phys. Rev. Lett. **109**, 107202 (2012)
[3] K. Horigane et al., J. Phys. Soc. Japan **76**, 114715 (2007)